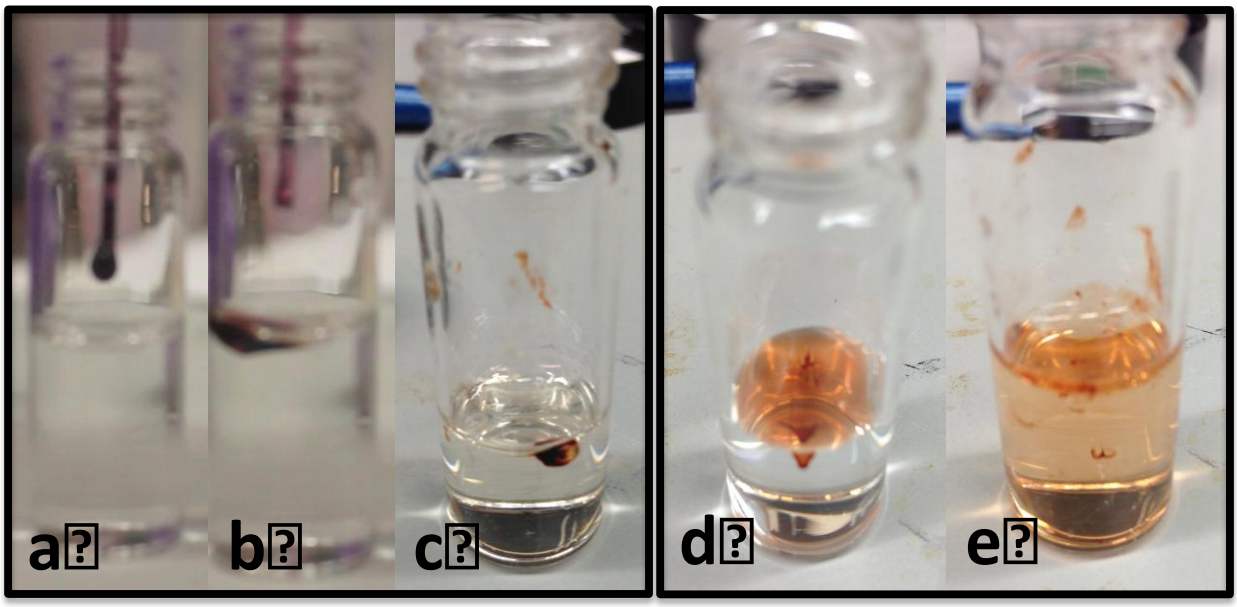
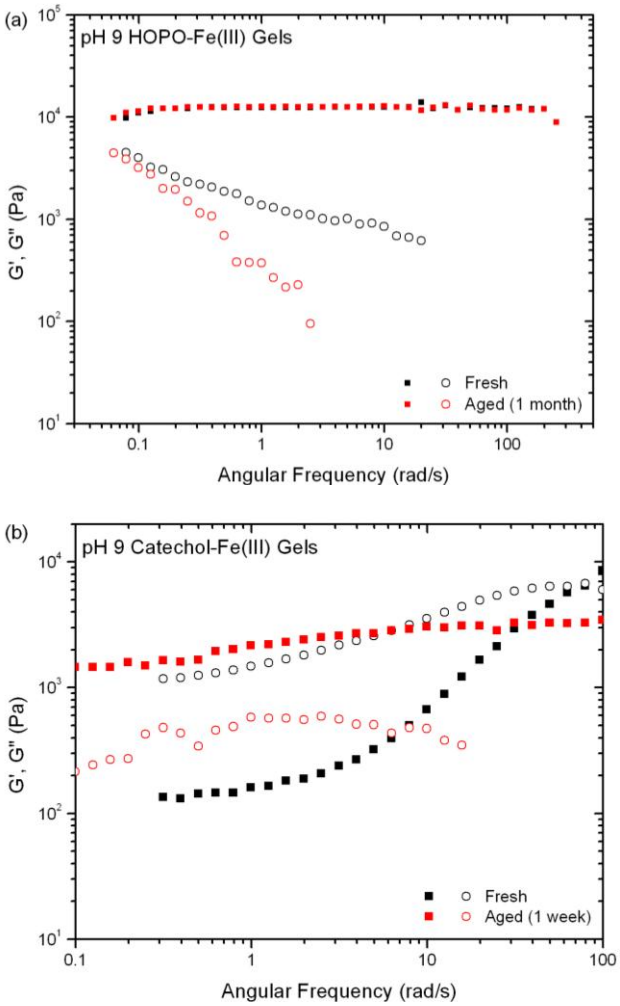
Supporting Information

Video file “HOPO Gel” attached in separate file

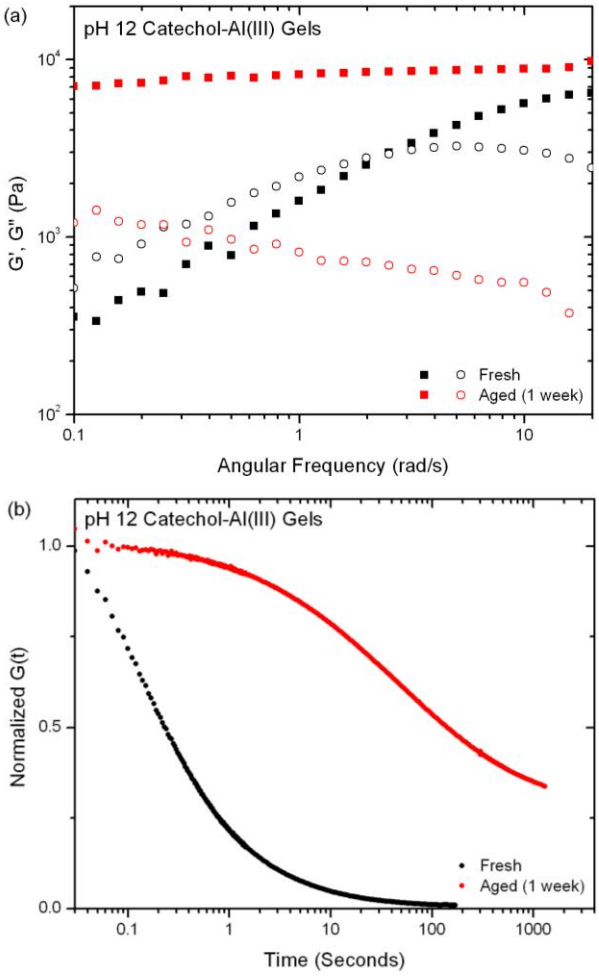
Supporting Video S1: Annotated video showing the gelation process for a 10% w/v HOPO-Fe(III) solution dropped into pH 7.4 phosphate buffer solution. The rapid set to a robust gel is evident. The limits of this strategy are tested by injection of a 5% w/v and 20% w/v solution through a 25 gauge needle into the same buffer solution.



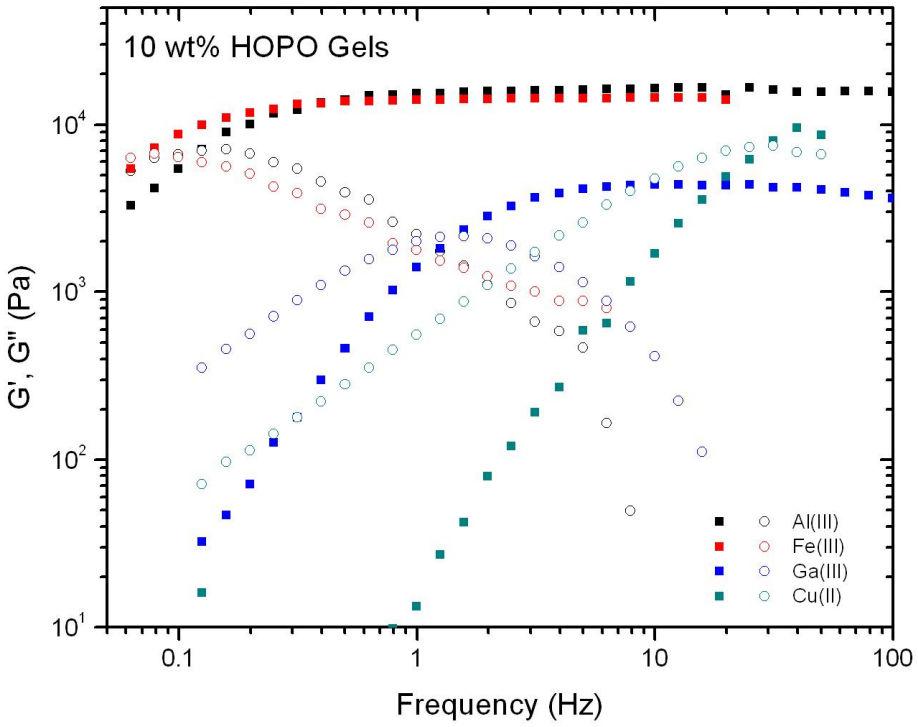
Supporting Figure S2: (a-c) Gelation process for a HOPO-Fe(III) hydrogel. (a) A 10% w/v solution of Fe(III)-bound HOPO is dropped into pH 7.4 phosphate buffer solution. (b) Gelation is immediately apparent, leading to minimal leaking of the injection solution. (c) The gel remains a separate phase even after subjection to a vortex mixer. (d-e) Gelation process for a nitrocatechol-Fe(III) hydrogel into pH 9 buffer solution. (d) Upon dropping, immediate spreading of the injection solution is clearly evident. (e) Vortex mixing leads to complete dissolution into the bulk.



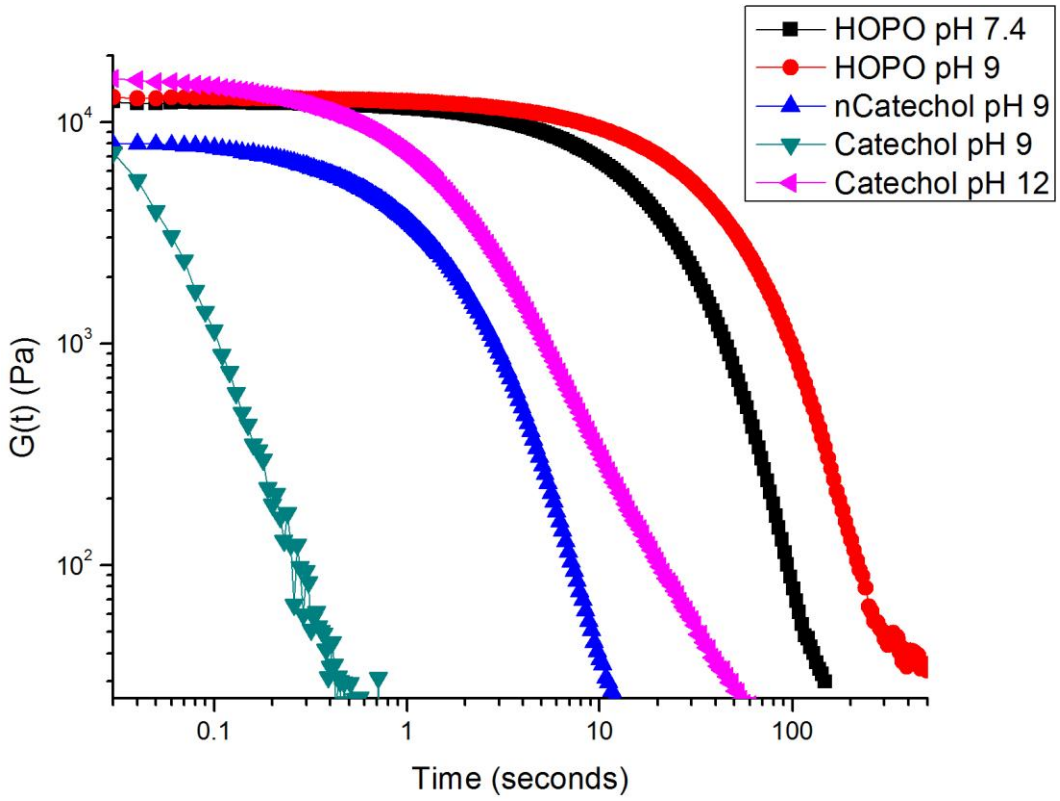
Supporting Figure S3: Dynamic oscillatory rheology of (a) pH 9 HOPO-Fe(III) gels as synthesized (black) and after 1 month storage on benchtop (red) and (b) pH 9 catechol-Fe(III) gels as synthesized (black) and after 1 week storage on the benchtop (red). Notable is the dramatic shift in rheological behavior for the catechol-Fe(III) hydrogel, compared to minimal change, even after an extended time frame for the HOPO-Fe(III) hydrogel.



Supplemental Figure S4: Rheological behavior of catechol-Al(III) shows a similar oxidation to that of the catechol-Fe(III) gels made at pH 12, signifying that the specific chemistry of the catechol-Fe(III) system is not required to promote covalent crosslinking, as Al(III) is not prone to redox reactions under the given conditions.



Supporting Figure S5: Dynamic oscillatory rheology comparison of hydrogels with HOPO and Al(III) (black), Fe(III) (red), Ga(III) (blue), and Cu(II) (green) at pH 7.4.



Supporting Figure S6: Stress relaxation data of HOPO, nitrocatechol and catechol-based Fe(III) hydrogels at the noted pH values after 20% strain. Characteristic of these dynamically crosslinked supramolecular hydrogels, all exhibit relaxation to a zero stress state. A version of this graph in which hydrogels have been normalized to initial modulus is shown in the main text as Figure 2b.

Comparison of theoretical maximum crosslink density and crosslink density calculated by rheological experiments.

The following equation can be used to calculate the maximum crosslink density in, for example, a pH 7.4 HOPO-Fe(III) hydrogel, assuming complete crosslink formation of all available chelating moieties.

$$\rho = \frac{Cf}{n}$$

where
ρ = crosslink density (moles crosslinks/cm^3)
C = concentration of PEG crosslinker
f = number of crosslink points per PEG crosslinker molecule
n = number of chains per crosslink

Here, C, the concentration of PEG crosslinker in a 10 wt% HOPO hydrogel is equal to 9.3 μmol/cm^3. The number of crosslink points, f, in a 95% HOPO-functionalized PEG crosslinker is equal to 4*0.95 = 3.8. As pH 7.4 HOPO-Fe(III) hydrogels are shown to be predominantly *tris* crosslinked, n = 3. This equates to a maximum theoretical crosslink density of 11.7 μmol/cm^3.

The crosslink density can be estimated from the plateau modulus observed during frequency sweep rheological experiments using the following equation from rubber elasticity theory:

$$\rho = \frac{G'_{plateau}}{RT}$$

Using a plateau modulus value of 12.5 kPa, as observed for pH 7.4 HOPO-Fe(III) hydrogels, a crosslink density of 5.0 μmol/cm^3 was calculated.

This 2-fold discrepancy in crosslink density is attributed to incomplete crosslink formation as well as the potential for coordination by two chelating functionalities on the same PEG crosslinker.